

# CHEMICAL REACTION IN TURBULENT FLOW SYSTEMS - THE ROLE OF THE MICROMIXING CONCEPT

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**SUMMARY** A transient response technique for measuring micromixing in a turbulent reacting flow system is described. A theoretical analysis confirms that a step-change in reactant feed composition results in a good discrimination between the limiting chemical conversions resulting from the extreme micromixing states of minimum mixedness and maximum mixedness. A micromixing index is defined, in terms of the limiting states, to quantify intermediate states of micromixing. The application of the technique to a jet-mixed reactor is then described. The paper concludes with a discussion of the significance of the work in the context of confined turbulent jet behaviour and of reactor design.

## 1 INTRODUCTION

Reacting flow systems are of particular importance in the chemical industry because the majority of chemical processing is carried out on a continuous basis. Reactants, either separately or in premixed form, are fed continuously into a bounded space where chemical transformation occurs, and the resulting mixture of products and unreacted reactants is simultaneously removed on a continuous basis for subsequent separation. The optimal design and operation of a chemical reactor therefore requires an understanding of the fluid mechanics of mixing in the system, on the one hand, the kinetics of the reaction taking place, on the other, and the interaction between the two.

In many instances of practical interest the flow is turbulent and the system geometry is complex, so that it has not been possible to predict the behaviour of the system by solving the relevant equations of momentum, energy and mass. That is not to imply that important progress has not been made, though, in applying this approach to particular cases, as instanced by the work initiated by Corrsin (1957) and carried on subsequently by others. An alternative approach emerged through the work pioneered by Danckwerts (1958), and later extended by Zwietering (1959), based on statistical distribution functions relating to the inlet fluid, the exit fluid, and the fluid inside the reaction space. The residence-time is the time spent in the reaction space by a element of inlet fluid, and the residence-time distribution describes the residence-times of a population of inlet fluid elements. For steady-flow conditions, the exit fluid has an identical residence-time structure. Similarly, the population of fluid elements in the reaction space is described in terms of an age distribution, and a life-expectation distribution relating, respectively, to the time since entry and the time before exit, of the various elements. These concepts are important because they provide information on the state of mixing in the system, and are readily measurable. A comprehensive account is given by Levenspiel (1972).

A knowledge of the degree of mixing in a reacting flow system, as characterized by the residence-time distribution, and of the kinetics of reaction, is not sufficient to predict the chemical conversion, except in the case of simple first-order reaction. Other reactions involve interaction between more than one reactant species at a molecular level, and the extent of reaction depends not only on the length of stay in the reaction space but also the extent of interaction of reactant species. First Danckwerts (1958), then

Zwietering (1959), and later McCord (1972) showed that chemical conversion could be predicted for limiting cases of the degree of species interaction, or 'micromixing' as it was termed. The upper and lower states of micromixing were termed 'maximum mixedness', and 'minimum mixedness', respectively.

The degree of micromixing in a particular reacting flow system is likely to fall between the two extremes, and so a considerable amount of work has been published on the development of mathematical models to describe intermediate degrees of micromixing. Essentially the models fall into two categories: 'coalescence-dispersion' models which are based on stochastic interactions between an ensemble of fluid elements, and 'multi-environment' models which assume that the reaction space can be divided into two or more discrete sub-regions, each having an extreme state of micromixedness. A recent paper by Mehta and Tarbell (1983) gives a useful summary of developments in this field. In contrast to the attention devoted to the development of mathematical models of micromixing, experimentally based studies are much less numerous. It seems clear that further progress in the application of micromixing theory depends critically on a thorough testing of proposed mathematical models with experimental data, and this demands more attention being given to the techniques of micromixing measurement.

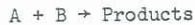
The available experimental work with premixed reactants has shown that experimental accuracy is a limiting factor in obtaining a sensitive evaluation of micromixing in a given reacting flow system. Theoretical predictions confirm that separate reactant stream systems provide greater potential sensitivity for comparable experimental accuracy, and the more recent work is proceeding along these lines. The paper by Mehta and Tarbell (1983) provides an up to date account of this approach.

The purpose of this paper is to describe a variant on the use of separate reactants as a means of measuring intermediate states of micromixing in a reacting turbulent flow system. In the case of a two reactant system instead of feeding the separate feed streams simultaneously into the reaction space, they are fed in sequentially, so that a step-change in feed composition occurs. The dynamic response in chemical conversion is then used to infer the state of micromixing in the reaction space. A theoretical analysis of this method is developed and a proposed index of micromixing is defined. The results of applying the technique to a jet-stirred reactor are described, and their significance assessed in terms of turbulent jet

behaviour. The paper concludes with a brief discussion of the wider potential of the method.

## 2 THEORY

Consider a liquid-phase reaction system involving an irreversible reaction between reactant species A and B, with simple second-order kinetics -



$$r = k.a.b. \quad \dots(1)$$

where

r is the reaction rate  
a is the concentration of A  
b is the concentration of B

A steady flow rate Q of feed containing reactant A in an inert solvent, with concentration  $a_f$ , passes into the reactor of volume V. At a certain instant of time,  $t=0$ , the feed composition undergoes a step-change in composition to a concentration  $b_f$  of reactant B in inert solvent. The reactor is operated isothermally at the feed temperature, and density is assumed to be independent of composition, so that the feed rate remains constant following the step-change. The dynamic response of chemical conversion will now be calculated for the extremes of micromixing, for a system with a known residence-time structure. The following analysis is based on the interpretation given by McCord (1972).

### 2.1 Minimum Mixedness

Consider the fluid emerging from the reactor at time  $t=u$ , where  $u>0$ . Since the condition of minimum mixedness assumes that inlet fluid elements remain totally segregated from other elements in passing through the reactor, there is no possibility of reaction between reactants A and B. All fluid elements which entered prior to  $t=0$  and emerge at  $t=u$  have residence times greater than  $u$ , and must contain only species A. Elements which entered after  $t=0$  and emerge at  $t=u$  have residence times less than  $u$ , and must contain only species B. When the various elements which make up the population of elements comprising the exit fluid at  $t=u$  are instantaneously mixed, the exit fluid composition is given by

$$\frac{a}{a_f} = 1 - F(u) \quad \dots(2a)$$

$$\frac{b}{b_f} = F(u) \quad \dots(2b)$$

where  $F(u)$  is given by the cumulative residence-time function of the flow system.

These solutions can be obtained directly by a simple material balance but it is useful to note that they would also result from a solution of the set of equations (3) to (7) given in the next section, with the rate constant  $k$  equal to zero. The response of the minimum mixedness system is therefore identical to that obtained from a step-change to a non-reacting tracer, which is the usual experimental method of determining the cumulative residence-time function  $F(u)$ .

### 2.2 Maximum Mixedness

The composition of the fluid emerging from the reactor at  $t=u$  can be regarded as the end result of an unsteady-state batch accretion and reaction process between fluid elements which entered prior to  $t=0$ , containing reactant A only, and fluid elements which entered between  $t=0$  and  $t=u$ , containing reactant B only. The batch is completely mixed at all times, so that when a fluid element joins the batch it is instantaneously dispersed within it at a molecular level. Thus in the interval  $t=0$  to  $t=u$ , reaction between A and B is possible, unlike the case of complete segregation or minimum mixedness. The accretion

process is schematically represented in Figure 1 and can be mathematically described as follows for  $t>0$  when reaction can occur -

$$\text{Overall} \quad v = 1 - F(u-t) \quad \dots(3)$$

$$q = \frac{dv}{dt} \quad \dots(4)$$

$$\text{Reactant A} \quad 0 = \frac{d}{dt}(v.a) + k.a.b.v \quad \dots(5)$$

$$\text{Reactant B} \quad q.b_f = \frac{d}{dt}(v.b) + k.a.b.v \quad \dots(6)$$

### Initial condition

$$t = 0, a = a_f, b = 0 \quad \dots(7)$$

### 2.3 Solutions

As an example, the dynamic response to a step-change in reactant feed of a reacting flow system, having a cumulative residence-time function described in equation (i) will be shown.

$$F(\theta_r) = 1 - (1+2\theta_r) \cdot \exp(-2\theta_r) \quad \dots(8)$$

where  $\theta_r$  is the non-dimensional residence-time (i.e. the residence-time normalized with respect to the mean residence time of the system).

For a given residence-time function, equations (3) and (4) enable  $q$  and  $v$  to be substituted into equations (5) and (6). These equations are then solved numerically to obtain the exit concentrations  $a$ ,  $b$  at time  $t=u$ . The equations can be made non-dimensional prior to solution by normalizing time with respect to mean residence-time and concentration with respect to feed concentration  $a_f$ ; this results in a non-dimensional reaction number  $K' = ka_f\tau$ , where  $\tau$  is the mean residence-time flow system. Figure 2 shows the responses expected for systems with a range of kinetics varying from slow to extremely fast ( $K = 0, 1, 10, \infty$ ), and equimolar concentrations of the reactant feeds A and B. The potential for discriminating between the extremes of micromixing is clearly evident.

### 2.4 Comparison with Premixed Feed Technique

The reason for choosing as an example in the previous section, a flow system with the cumulative residence-time function described by equation (8), is that it enables a comparison to be made between the proposed step-change technique and the premixed feed technique. The results given in the paper by Zwietering (1959) include this flow system as a specific example, with an equimolar premixed feed containing A and B. For a non-dimensional reaction number  $K=10$ , the results show that the respective steady-state non-dimensional exit concentrations of B for maximum and minimum mixedness are 0.196 and 0.140, a difference of 0.056 non-dimensional concentration units. Figure 2 shows that with the step-change technique differences as large as 0.35 non-dimensional concentration units can be obtained for a corresponding  $K$  number. The relative advantage of the step-change method is quite marked, and this is further reinforced by the need to run the premixed feed experiments at steady-state to obtain the maximum difference between the extremes of micromixing - as can readily be demonstrated by calculation. In consequence there could be a significant difference between the methods in the time required to carry out the necessary experimental work.

## 3 APPLICATION

The proposed method for measuring micromixing using a step-change in reactant feed is being used to study a jet-stirred reaction system. Previous work carried out by Wood (1968) (1971) (1974) had established a cumulative residence-time relationship for jet-stirred

cylindrical vessels. The observed residence-time structure was explained in terms of a model based on the known mean-flow properties of a bounded turbulent jet in the form of a jet-stirred reactor.

### 3.1 Experimental

The experimental reactor consists of a perspex cylindrical vessel with interchangeable axial inlet and exit nozzles, similar to those used in the residence-time work. A second-order irreversible reaction system involving aqueous solutions of sodium hydroxide (reactant A) and crystal violet (reactant B) was chosen for study for the following reasons: the reaction can be monitored continuously using spectrophotometry; significant reaction occurs at ambient temperatures; heat effects are negligible; and rate constants obtained by Corsaro (1964) are available for checking purposes.

An experimental run was carried out by filling the reactor with sodium hydroxide solution and establishing a steady flow through it, and then introducing a step-change to the solution of crystal violet. The exit stream from the reactor was monitored continuously by bypassing some of it through a continuous flow cell attachment to a spectrophotometer. Calibration curves were previously prepared, relating the absorbance and crystal violet concentration. In this way the dynamic response of chemical conversion to the step-change in reactant feed was obtained.

### 3.2 Results

The results from a typical experimental run are presented below.

Vessel diameter: 146 mm; Flow rate: 0.6 litres/min  
 Vessel length: 152 mm; Mean residence-time: 4.26 min  
 Nozzle diameter: 2.175 mm; Jet Reynolds number: 4000  
 Feed concentration A:  $3.89 \times 10^{-2}$  M  
 Reaction rate constant: 11.5 litre/mol.min  
 Reaction temperature: 25°C

Response data: given as time in min and exit concentration B normalized with respect to feed concentration B.

Time	Exit B	Time	Exit B
1	0.208	6	0.617
2	0.314	7	0.679
3	0.407	8	0.734
4	0.481	9	0.786
5	0.552	10	0.831

## 4 DISCUSSION

Figure 3 enables a comparison to be made between the experimental results obtained with the jet-mixed reactor operating under the conditions listed in the previous section, and the predicted performance of a similar reactor operating at the extremes of micromixing. The limiting curves were calculated using the residence-time function given below from a relationship proposed by Wood (1968) -

$$F(t) = 1 - K \cdot \exp - K \frac{(t-t^*)}{(\tau-t^*)} \cdot H(t-t^*) \quad \dots(9)$$

where H is the Heaviside function and K, t\* are parameters which can be calculated from the geometry of the flow system

For the reactor used in this experiment, K is 0.91 and t\*/ $\tau$  is  $3 \times 10^{-3}$ . The proposed method clearly has the potential to discriminate adequately between the

extremes of micromixing. Arising from this is the important question of quantifying the state of micromixing arising from a particular reacting flow system. One possibility would be to pursue the existing approaches based on the 'coalescence-dispersion' models and the 'multi-environment' models, referred to earlier. Without diminishing the importance of either, they both entail substantial computation to implement; for this reason a simpler alternative is put forward in this paper.

### 4.1 A Micromixing Index

Consider a micromixing index I which varies between 0 and 1, representing the extremes of minimum mixedness and maximum mixedness, respectively. This index can be related to an effective non-dimensional reaction number K' for the system as follows -

$$I = \frac{(K')_{\text{system}}}{(K')_{\text{maximum}}} \quad \dots(10)$$

The K' for a given system can be calculated from the experimental measurement of conversion. As an example, for the jet-mixed reactor experiment the measured non-dimensional concentration of reactant B at unit non-dimensional time is 0.50. This is also the value which would result from a maximum mixed system with a non-dimensional reaction number of 0.73. Therefore the jet-mixed system has an effect K' of 0.73 and a micromixing index of 0.38, based on a K' value of 1.91 for the maximum mixed limit.

### 4.2 Significance of the Micromixing Index

The proposed micromixing index I reflects the reduced reaction capability of a reacting system caused by limitations on the interaction between reactant species at a molecular level. It has the advantage of being readily determined from the experimental measurements, and is simpler than the previously proposed approaches to quantifying intermediate states of micromixing. The next phase of this work involves the application of this concept to a detailed study of the micromixing in a jet stirred reactor. The results will hopefully provide additional information on the mechanisms operating in a confined turbulent jet, and the possibility of relating the micromixing index to the microscale parameters of the turbulent field.

## 5 CONCLUSIONS

1. A proposed method for measuring micromixing in a reacting flow system provides excellent discrimination between the limiting states of minimum mixedness and maximum mixedness.
2. The experimental procedure is straight forward and non time consuming, as is demonstrated for a jet-mixed reaction system.
3. A micromixing index is proposed which appears to be simpler than alternative methods of quantifying micromixing. It is hoped that the method will provide additional information which can be used to elucidate the mechanisms operating in a turbulent flow field.

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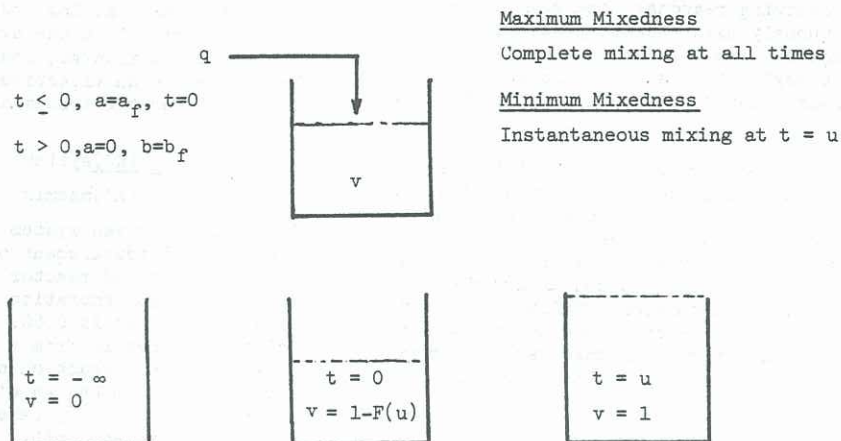


FIGURE 1 McCord's Model of Minimum and Maximum Mixedness

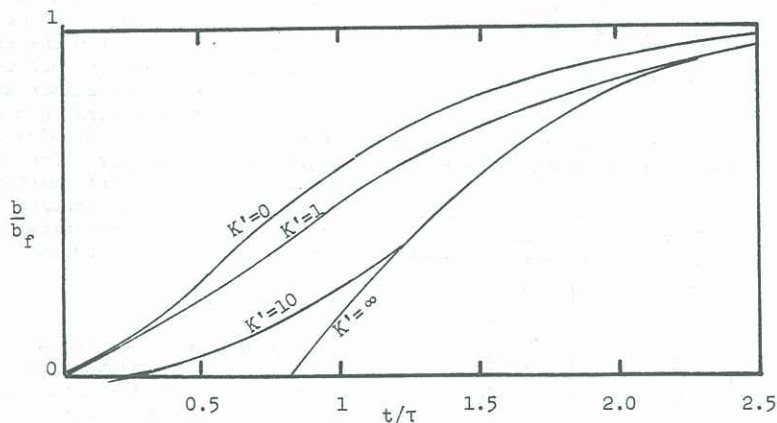


FIGURE 2 Step Response for Various Reaction Numbers

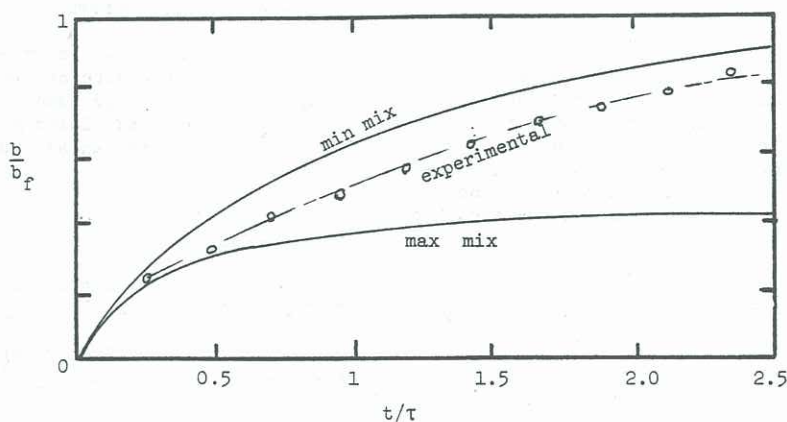


FIGURE 3 Experimental Response for Jet-Mixed System